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(21) International Application Number: PCT/FI91/00349 (22) International Filing Date: 22 November 1991 (22.11.91) (30) Priority data: 905797 23 November 1990 (23.11.90) FI (71) Applicant (for all designated States except US): PAROC OY AB [FI/FI]; SF-21600 Pargas (FI). (72) Inventors; and (75) Inventors/Applicants (for US only) : KARPPINEN, Kirsti, Marjatta [FI/FI]; Stoltgatan 8 B 26, SF-20350 Åbo (FI). PERANDER, Michael, Stig, Folke [FI/FI]; Väderkvarnsvägen 10, SF-21600 Pargas (FI). SOLIN, Peter, Arnold, Henrik [FI/FI]; Revonkatu 3-5, SF-20760 Piispanristi (FI). PEHKONEN, Antero, Olavi [FI/FI]; Rönträdsvägen 7 A 1, SF-02940 Esbo (FI). MAINE, Seija, Marketta [FI/FI]; Tummelvägen 14 bost. 3, SF-21600 Pargas (FI).		(74) Agent: OY JALO ANT-WUORINEN AB; Skepparebrinken 2 A, SF-00120 Helsingfors (FI). (81) Designated States: AT (European patent), AU, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LU (European patent), ML (OAPI patent), MR (OAPI patent), NL (European patent), NO, PL, RO, SE (European patent), SN (OAPI patent), SU*, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i>
(54) Title: MINERAL FIBRE COMPOSITION (57) Abstract A mineral fibre composition which is soluble in biological fluids contains substantially 45-65 % by weight of SiO ₂ , 15-40 % by weight of CaO, 0-20 % by weight of MgO, 0-6 % by weight of Na ₂ O + K ₂ O, and in addition aluminium and/or iron oxides as well as phosphorus oxide in such amounts that the weight ratio of P ₂ O ₅ to the sum of Al ₂ O ₃ and iron oxide is circa 0.4 to 6.		

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Mineral fibre composition

The present invention relates to a mineral fibre composition which is soluble in biological fluids.

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Mineral fibres made by melting and spinning of mineral raw materials, such as rock, slag and the like, are to a great extent used for the manufacture of mineral fibre mats and blankets, primarily for heat and sound insulation purposes within the construction industry. In addition to the formed mat exhibiting good insulation characteristics with respect to heat and sound, increasingly more importance has been recently attached to the characteristics of the mat from the viewpoint of health, primarily of industrial hygiene. This has lead to attention being directed increasingly more to developing fibres which are soluble in biological fluids in order to ensure that fibre particles, which are not transported out of the body, dissolve in the body fluid.

Thus e.g. the patent application WO 89/12032 describes a fibre composition which exhibits an increased solubility in physiological saline solutions. According to the specification, the components in the said compositions may vary within wide limits, but according to the specification, an increase in the amount of amphoteric oxides, i.a. of aluminium, zirconium and titanium, tends to increase the stability of the compositions against extraction. Even though the application does not at all discuss the effects of the presence of phosphorus, there is included an example of a composition containing a little over 6 % by weight of P_2O_5 , in combination with a low content of Al_2O_3 . This composition exhibits a fairly good solubility, primarily due to the small amount of Al_2O_3 present.

According to the invention it has now been discovered that compositions which contain aluminium and/or iron oxides, as well as phosphorus oxide, and wherein the weight ratio of phosphorus to the sum of aluminium and iron, all calculated

as their oxides, lies within a fairly narrow range, surprisingly exhibit very favourable solubility characteristics in physiological saline solutions.

- 5 The object of the present invention is thus a mineral fibre composition which is soluble in biological fluids and which is characterized in that it contains substantially

10 45-65 % by weight of SiO_2
15-40 % by weight of CaO
0-20 % by weight of MgO
0-6 % by weight of $\text{Na}_2\text{O} + \text{K}_2\text{O}$

15 and in addition aluminium and/or iron oxides as well as phosphorus oxide in such amounts that the weight ratio of P_2O_5 to the sum of Al_2O_3 and iron oxide is circa 0.4 to 6.

20 The total amount of Al_2O_3 and iron oxide is preferably at least circa 0.5, advantageously circa 0.5 to 7 % by weight and the said weight ratio is preferably circa 0.5 to 2.

25 The object of the invention is also a method for increasing the solubility of mineral fibre compositions which method is characterized in that to a mineral composition having a total Al_2O_3 and iron oxide content of at least circa 0.5 % by weight, phosphorus is added in such an amount that the weight ratio of P_2O_5 to the sum of Al_2O_3 and iron oxide is circa 0.4 to 6, optimally circa 0.5 to 2.

30 The invention thus makes it possible to utilize such common natural and economically feasible raw materials which generally contain a certain amount of aluminium and iron, which reduce the solubility and the presence of which
35 consequently is not desirable in the manufacture of a soluble fibre. According to the invention the solubility of

fibres made from such materials is increased by adding phosphorus in a suitable amount. This increases substantially the variation possibilities in the choice of raw materials whereby also economically advantageous raw materials can come into use.

The upper limit of added phosphorus oxide, which generally does not exceed circa 10 % by weight of the composition, depends naturally on the aluminium and iron content and also on the fact that higher phosphorus oxide levels contribute to an undesired crystallization of the fibre and difficulties in raw material supply. An increase of the phosphorus oxide content also raises the melting temperature which leads to even poorer production economics.

In order for mineral fibre to be bioactive or soluble in biological fluids, a layer of calcium phosphate or apatite type material has to be formed on the surface of the fibre. This outer layer is a result of migration of calcium and phosphate ions from the glass matrix outwards to the surface directed towards the biological fluid, which surface layer formation is further facilitated by the phosphate ions present in the biological fluid.

This formed layer gradually then separates in the form of very small particles thus exposing new fibre surface onto which new surface layers then can form. The glass matrix gradually being leached, the fibre disintegrates and disappears.

The presence of trivalent aluminium and iron has a stabilizing effect on the leaching of the glass matrix due to the fact that these metals tend to move to disrupted oxygen bridges in the glass, where the deterioration and leaching reactions of the glass take place. The phosphate ions, however, form complexes with these trivalent metal ions and weaken the oxygen bridges between the Si- and Al- and Fe-

atoms, respectively. As a consequence of this, the network forming properties of these metals weaken in turn, which facilitates the breaking down of the glass.

- 5 The present invention is consequently based on a joint effect between phosphate and aluminium and trivalent iron, respectively, which cooperation in the mineral fibres according to the invention increases the solubility of the fibre.

10 In the following, when iron oxide is expressed as Fe_2O_3 , this expression is intended to cover all types of iron oxides Fe_xO_y present in the composition.

- 15 An advantageous fiberizable mineral fibre composition contains the following components at the amounts indicated:

	SiO_2	45-65	% by weight
	Al_2O_3	0.5-7	"-
20	Fe_2O_3	0-5	"-
	CaO	15-40	"-
	MgO	0-20	"-
	$\text{Na}_2\text{O} + \left. \begin{array}{l} \text{K}_2\text{O} \end{array} \right\}$	0-6	"-
25	P_2O_5	0.5-10	"-

An especially advantageous composition has the following composition:

	SiO_2	49-56	% by weight
30	Al_2O_3	1-5	"-
	Fe_2O_3	0-4	"-
	CaO	25-35	"-
	MgO	0-15	"-
	$\text{Na}_2\text{O} + \left. \begin{array}{l} \text{K}_2\text{O} \end{array} \right\}$	0-6	"-
35	P_2O_5	0.5-5	"-

Solubility tests

1. Solubility in a Gamble solution

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In order to test the solubility, mineral fibre compositions according to the invention were compared with corresponding compositions which, however, contained no phosphate.

10

From quartz sand, calcium carbonate, Al-, Mg- and P-compounds a melt was prepared which after solidification was crushed and pulverized. The chemical composition was controlled, as was the particle size distribution. A specimen of 200 ml was rinsed with a Gamble solution having a flow rate of 2 ml/h. The Gamble solution had the following composition:

	MgCl ₂ * 6H ₂ O	0.16 g/l
20	NaCl	6.11 g/l
	KCl	0.31 g/l
	Na ₂ HPO ₄	0.148 g/l
	Na ₂ SO ₄	0.079 g/l
	CaCl ₂ * 2H ₂ O	0.06 g/l
25	NaCH ₃ COO * 3H ₂ O	1.065 g/l
	NaHCO ₃	1.95 g/l

The rate of dissolution was determined by measuring the concentrations of the main components of the material in the Gamble solution after specific time intervals. An atomic absorption spectrophotometer was used for the determinations.

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Composition (% by weight)

		Ia	Ib	IIa	IIb
5	SiO ₂	55.2	58.8	54.1	54.2
	Al ₂ O ₃	1.2	1.2	4.2	4.4
	Fe ₂ O ₃	0.1	0.05	0.05	0.0
	CaO	29.3	30.2	27.7	30.2
	MgO	10.2	9.7	9.7	10.4
10	Na ₂ O	0.1	0.03	0.09	0.1
	K ₂ O	0.0	0.02	0.02	0.02
	P ₂ O ₅	1.7	-	3.9	-

15 Solubility (mg/l) (1 day)

		Ia	Ib	IIa	IIb
	Si	62.2	58.6	34.5	32.1
20	Ca	27.8	27.7	22.7	30.3
	Mg	16.5	14.0	13.4	14.5

From the results it can be seen that the compositions Ia and IIa according to the invention which contained phosphate, had a better silicon solubility than the corresponding compositions Ib and IIb which were phosphate free. Magnesium and calcium solubilities remained rather constant.

30 2. Solubility in cultur media with or without macrophages

In this test the dissolution of three mineral fibre compositions were tested on the one hand in a commercial culture medium (RPMI 1640 Medium, Gibco Ltd, England) and also in the same culture medium containing in addition macrophages. The latter medium was prepared by suspending rat alveolar macrophages, the viability of which was over

95%, in a RPMI 1640 medium containing pencillin 100 IU/ml, streptomycin 100 μ g/ml, 10 IU/ml heparin, 10% foetal calf serum and 2 mM L-glutamine, to a cell concentration of 1×10^6 cells/ml. 2 ml of cell suspension was added to and
 5 incubated in each well of Costar tissue culture clusters (Costar Europe Ltd, Holland), changing the medium to remove non-adherent cells, and incubated overnight. Following incubation, the medium was removed and fresh medium containing 200 μ g/ml of mineral fibres were added to the
 10 wells. In control wells, only RPMI 1640 Medium with 200 μ g/ml of mineral fibre was used. The clusters were incubated and the cells exposed to fibres for a predetermined time. The concentration of dissolved silicon from each of the samples was determined from the culture medium using
 15 atomic absorption spectrofotometer.

Fibre compositions (% by weight)

		A	B	C
20	SiO ₂	54.7	50.4	59.0
	Al ₂ O ₃	1.7	3.3	0.9
	Fe ₂ O ₃	1.4	3.0	0.3
	CaO	25.1	31.2	35.5
	MgO	11.9	10.6	4.6
25	Na ₂ O	0.3	0.6	0.1
	K ₂ O	0.1	0.4	0.1
	P ₂ O ₅	5.2	-	-

Composition A is in accordance with the invention, compositions B and C otherwise fulfill the conditions of the
 30 invention, except that they do not contain any phosphorus.

The diameter of the fibres used in the tests was less than 3 μ m.

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The following solubility results for silicon were obtained

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after 2 days, 4 days and 8 days respectively.

<u>Composition</u>		<u>A</u>	<u>B</u>	<u>C</u>
		<u>Si (ppm; 2 days)</u>		
5	Culture medium	26	5	26
	"- + macrophages	26	5	14
		<u>Si (ppm; 4 days)</u>		
	Culture medium	45	12	45
10	"- + macrophages	45	8	35
		<u>Si (ppm; 8 days)</u>		
	Culture medium	162	45	144
	"- + macrophages	153	37	82

15 From the results it is apparent that the solubility of the composition B, which has a relatively high total content of aluminium and iron oxides, is very low. The composition C, which has a very low total content of aluminium and iron oxides, has a high solubility in culture medium, but a
20 significantly lower solubility in a culture medium containing macrophages.

Fibre A, however, which is according to the invention and which has a considerably higher total aluminium and iron
25 oxide content than the composition C, and which also contains phosphorus, has the same high solubility as the composition C in plain culture medium but, in addition, a correspondingly high solubility also in a culture medium containing macrophages.

30 The results thus show that in the compositions according to the invention, phosphorus has a solubility increasing effect which is especially pronounced in conditions resembling the true biological conditions in the organism.

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Claims

- 5 1. A mineral fibre composition which is soluble in biological fluids, **characterized** in that it contains substantially

10 45-65 % by weight of SiO_2
15-40 % by weight of CaO
0-20 % by weight of MgO
0-6 % by weight of $\text{Na}_2\text{O} + \text{K}_2\text{O}$

15 and in addition aluminium and/or iron oxides as well as phosphorus oxide in such amounts that the weight ratio of P_2O_5 to the sum of Al_2O_3 and iron oxide is circa 0.4 to 6.

- 20 2. Mineral fibre composition according to the Claim 1, **characterized** in that the weight ratio of P_2O_5 to the sum of Al_2O_3 and iron oxide is circa 0.5 to 2.

- 25 3. Mineral fibre composition according to the Claim 1 or 2, **characterized** in that it contains Al_2O_3 and iron oxide in a total amount of at least 0.5 % by weight.

4. Mineral fibre composition according to the Claim 3, **characterized** in that it contains Al_2O_3 and iron oxide in a total amount of 0.5 to 7 % by weight.

- 30 5. Mineral fibre composition according to the Claim 1, **characterized** in that it has substantially the following composition:

		10	
	SiO ₂	45-65	% by weight
	Al ₂ O ₃	0.5-7	"-
	Fe ₂ O ₃	0-5	"-
	CaO	15-40	"-
5	MgO	0-20	"-
	Na ₂ O +		
	K ₂ O }	0-6	"-
	P ₂ O ₅	0.5-10	"-

10 6. Mineral fibre composition according to the Claim 5, characterized in that it has substantially the following composition:

	SiO ₂	49-56	% by weight
15	Al ₂ O ₃	1-5	"-
	Fe ₂ O ₃	0-4	"-
	CaO	25-35	"-
	MgO	0-15	"-
	Na ₂ O +		
20	K ₂ O }	0-6	"-
	P ₂ O ₅	0.5-5	"-

25 7. Method of increasing the solubility in a biological fluid of a mineral fibre material, characterized in that to a mineral fibre composition having a total content of Al₂O₃ and iron oxide of at least circa 0.5 % by weight, phosphorus is added in such an amount that the weight ratio of P₂O₅ to the sum of Al₂O₃ and iron oxide is circa 0.4 to 6.0, optimally circa 0.5 to 2.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 91/00349

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 03 C 13/00, 3/087, 3/097										
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 03 C</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p style="padding: 5px;">SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 03 C				
Classification System	Classification Symbols									
IPC5	C 03 C									
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category *</th> <th style="width: 60%; padding: 5px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; padding: 5px;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A,P</td> <td style="vertical-align: top; padding: 5px;">EP, A1, 0412878 (ISOVER SAINT-GOBAIN) 13 February 1991, see the whole document -----</td> <td style="vertical-align: top; padding: 5px;">1-7</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A,P	EP, A1, 0412878 (ISOVER SAINT-GOBAIN) 13 February 1991, see the whole document -----	1-7		
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A,P	EP, A1, 0412878 (ISOVER SAINT-GOBAIN) 13 February 1991, see the whole document -----	1-7								
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>										
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 5px;">11th February 1992</td> <td style="padding: 5px;">1992 -02- 3</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 5px; text-align: center;">SWEDISH PATENT OFFICE</td> <td style="padding: 5px; text-align: center;"> May Hallne </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	11th February 1992	1992 -02- 3	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	 May Hallne
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ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00349**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 30/11/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0412878	91-02-13	AU-D- 6002590	91-02-14
		CN-A- 1049834	91-03-13
		FR-A-B- 2650821	91-02-15
		JP-A- 3093650	91-04-18
		FR-A- 2658182	91-08-16